

# C E M E N T

AND

## CEMENT MANUFACTURE

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### Czechoslovakian Standard Specifications for Cements.

The following is an abstract of the Standard Specification for Portland Cement issued by the Ministry of Public Works of Czechoslovakia in July, 1934.

#### Portland Cement.

**DEFINITION.**—Portland cement is a powdered hydraulic binding material prepared by sintering raw material containing principally lime, alumina, and silica. In the finished cement, for every one part by weight of silica, alumina and iron oxide ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ) there must be at least 1.7 parts by weight of lime ( $\text{CaO}$ ). For regulating the quality of Portland cement, gypsum may be added up to a maximum of 2.5 per cent.  $\text{SO}_3$  in the finished cement. No other additions may be made. The insoluble residue may not be more than 2 per cent. nor the  $\text{MgO}$  content more than 5 per cent. These figures are to be obtained on the ignited cement.

**DELIVERY AND TESTING.**—Portland cement must be sold by weight. For sacks the standard weight is 50 kg. and for barrels 200 kg., and variations must not exceed 2 per cent. The weight of packing for sacks must not exceed 1.5 per cent. and for barrels 6 per cent. of the total weight.

Each sample for testing must weigh at least 15 kg. and consist of a number of samples (well mixed together) taken from various parts of the cement container. For delivery by railway the samples must be taken in amounts of about 1.5 kg. at a time for barrels and 0.75 kg. at a time for sacks, and for every 30,000 kg. a 15-kg. sample must be obtained.

If the samples for sufficient reasons cannot be obtained as described, they may be obtained from the works storage bins. For every 30,000 kg., soundness, setting time, and fineness tests must be made at the cement works. For every 100,000 kg. a tensile and compressive strength test must also be made. The cement must be kept in a closed dry room and tested not later than three months from the date of delivery.

**SETTING TIME.**—Slow-setting cement must not begin to set before 60 minutes after adding the gauging water and the setting must be complete within 15 hours. If the cement begins to set before 60 minutes but not before 30 minutes, it is to be classed as medium-setting. The specification does not apply to cements with setting times outside these limits. The Vicat needle test is to be used and the test carried out on paste of normal consistency as described in other specifications.

**SOUNDNESS.**—Portland cement must be volume-constant in air and water. Soundness is determined partly by testing a pat of cement after 28 days water storage and partly by the accelerated test in which the pat of cement paste is boiled. The results of both tests are decisive. Two pats are to be made from cement paste containing 1 per cent. more water than that required for normal consistency. A quantity of 200 g. is used for this purpose and the paste is spread on two glass plates so that two pats are obtained about 10 cm. in diameter and about 1 cm. thick at the middle sloped off towards the rim. For the accelerated soundness test two pats similarly prepared are placed immediately after making in a closed box containing damp air at 15 to 20 deg. C. As soon as the pats have set, and at the earliest 24 hours after making, they are put either with or without the glass plates into water at 15 to 20 deg. C. which is then slowly heated during about 60 minutes to boiling and kept at boiling point for three hours. The pats should show no crazing, crumbling, or disintegration.

**FINENESS.**—There must not be more than 2 per cent. residue on a sieve with 900 meshes per sq. cm. having wires of 0.1 mm. diameter, and not more than 20 per cent. on a sieve with 4,900 meshes per sq. cm. having wires of 0.05 mm. diameter.

**STRENGTH.**—Strength tests are to be carried out on standard mortar consisting of one part of cement and three parts of standard sand by weight. The tensile specimens must be 8-shape with a minimum cross section of 5 sq. cm. (width 2.22 cm., length 2.25 cm.). Compression specimens must be cubes with a cross section of 50 sq. cm. (7.07 cm. sides). Specimens must be kept in a closed box in damp air for 24 hours after making. One batch must be placed in water and the other kept 6 days in water and then 21 days in air. The temperature of the water and the air during storage must be 15 to 20 deg. C. and the relative humidity 50 to 80 per cent. For ordinary Portland cement the results of the tensile and compressive strength tests after 7 and 28 days water storage and after 28 days combined storage are decisive. For high-early-strength Portland cement the results after 3, 7, and 28 days water storage and after 28 days combined storage are decisive. The specimens must be tamped 150 times with a mechanical hammer of 2 kg. weight falling a height of 168 mm.

The specimens must be prepared as follows: 250 g. of cement and 750 g. standard sand are mixed dry in a dish for one minute and then mixed with 8 per cent. (80 g.) water. The mass should be stirred for one minute with a spoon, spread uniformly on the table of the mixing machine, and mixed by 24 turns of the table during three minutes. Of this mixture, 800 to 860 g. are placed in

a slightly-oiled cube mould and struck with the Böhme hammer. If after 90 to 100 blows water appears at the spaces in the mould the amount of water used is correct ; if this is not so, the amount of water is altered until the desired result is obtained, and the amount of water so obtained is to be used for all the specimens. At least five specimens must be made for each test. The minimum allowable strengths are given in Table I.

TABLE I.

Storage of specimens. Type.	Allowable minimum strength in kg. per sq. cm. of standard specimen.			
	Ordinary Portland cement.		Early-high-strength Portland cement.	
	Compression.	Tensile.	Compression.	Tensile.
1 day in damp air in closed box followed by :—				
2 days in water .. .. .	—	—	275	25
6 days in water .. .. .	200	18	375	28
27 days in water (water storage) ..	275	25	425	30
6 days in water, 21 days in air (combined storage) .. .. .	350	30	500	40

**STANDARD SAND.**—The sand must be natural quartz sand which has been cleaned mechanically and dried, and which is retained between sieves with holes of 1.35 mm. and 0.775 mm. diameter ; the sieves must be made of 0.25 mm. thick brass sheet.

#### Iron Portland Cement.

Iron Portland cement contains at least 70 per cent. Portland cement and at most 30 per cent. basic blastfurnace slag obtained during the manufacture of iron and granulated by rapidly cooling the molten material. The slag must be ground with the cement. The Portland cement used must fulfil the requirements of the standard specification for Portland cement. The blastfurnace slag should have for every one part ( $\text{SiO}_2 + \frac{2}{3}\text{Al}_2\text{O}_3$ ) at least one part ( $\text{CaO} + \text{MgO} + \frac{1}{3}\text{Al}_2\text{O}_3$ ). It must not contain more than 5 per cent.  $\text{MnO}$ . Additions for regulating the quality of the cement must not exceed 3 per cent. of the weight. The residue on the 900-mesh sieve must not exceed 2 per cent. and that on the 4,900-mesh sieve 20 per cent. In other respects the cement must conform to the specification for Portland cement.

#### Blastfurnace Cement.

Blastfurnace cement contains at least 20 per cent. Portland cement and at most 80 per cent. basic blastfurnace slag. The residue on the 900-mesh sieve must not exceed 1 per cent. and that on the 4,900-mesh sieve 12 per cent. In other respects the cement must conform to the specification for iron Portland cement.

#### Aluminous Cement.

Aluminous cement may be prepared by melting or sintering the raw materials and grinding them to a fine powder. The insoluble residue shall not exceed 2 per cent. The setting time is to be determined on cement paste of normal

consistency by following the temperature rise of the paste, and the end of the setting is the time when the temperature reaches a maximum and then begins to drop. The test is to be carried out in a hard rubber ring as used for the setting-time test on Portland cement. A thermometer is placed in the paste in such a manner that the mercury is completely immersed and its lower end is 1 cm. above the glass baseplate. The test must be carried out at a temperature of 15 to 20 deg. C. and a relative humidity of 50 to 80 per cent. in a room free from draughts. The 3-day tension and compression tests are decisive. The minimum allowable strengths in kg. per sq. cm. are given in Table II.

TABLE II.

	Compression.	Tension.
Water storage :		
After 1 day .. .. .	450	25
" 3 days .. .. .	550	28
" 28 " .. .. .	650	33
Combined storage :		
After 28 days .. .. .	700	35

In other respects the cement must conform to the standard specification for Portland cement.

## Russian Standard Specifications for Cements.

### Portland Cement.

A SPECIFICATION for Portland cement was issued by the All-Union Select Committee on June 14, 1932, and came into force on August 1, 1932. The following is an abstract of the specification :

Portland cement is made by sintering and grinding materials containing calcium carbonate and clay. Other materials, such as blast-furnace slag and diatomaceous earth of suitable composition may be used. Gypsum may be added in amounts not exceeding 3 per cent. Hydraulic materials such as those used in slag and pozzolana cements may be added in amounts up to 10 per cent. According to the strengths three classes of Portland cement are recognised, "o," "oo," and "ooo" (high strength). In the finished product the  $\text{SO}_3$  content must not exceed 2.5 per cent., the  $\text{MnO}$  4.5 per cent., the loss on ignition 4 per cent.

*Setting Time.*—Initial setting time by the Vicat needle must not be less than 30 minutes and final setting time not longer than 12 hours.

*Fineness.*—Minimum finenesses on the 900-mesh per cm.<sup>2</sup> sieve are 2% residue for types "o" and "oo," and 1 per cent. for type "ooo"; on the 4900-mesh sieve 25 per cent. residue for types "o" and "oo" and 15 per cent. for type "ooo."

*Soundness.*—Paste of normal consistency is prepared from 800 g. of cement and rolled with the hands into six balls of about 4 cm. diameter each. These are placed on glass plates covered with moist filter paper. The plates are jarred

on a hard surface until the balls form pats about 7 cm. in diameter and 1 cm. thick in the middle. The tops of the pats are smoothed with a wet knife. The six pats are kept 24 hours in an atmosphere saturated with water vapour. Two pats are then put into water for 27 days. The other four pats are placed in a water bath, two in the water and two on a shelf above water level. The water is brought to the boil and kept at boiling point for four hours. The pats are then allowed to cool in the bath till the next day. The pats must show no crazing or bending.

*Specific Gravity.*—No limits are indicated.

*Normal Consistency.*—The Vicat needle is to be 1 cm. in diameter and the total weight on it 300 g. A paste of 400 g. of cement worked up with 80 to 120 g. water is made and filled into the mould. Mixing may be carried out by hand or in a Werner and Pfleiderer mixer. When the needle sinks through the cement paste to 5 to 7 mm. of the glass plate the consistency is taken as normal.

*Packing.*—Barrels must be of uniform weight, 155 kg. net (about 165 kg. gross) and 170 kg. net (about 180 kg. gross). Paper sacks must weigh 50 kg. net.

*Normal Consistency of Mortar.*—200 g. of cement and 600 g. of standard sand are mixed for one minute dry and one minute wet in a metal bowl. The mortar is then put in a Steinbrück-Schmelzer mixer and mixed for 20 revolutions, or a Werner and Pfleiderer or other mixer of  $\frac{1}{2}$ -litre capacity may be used. The mortar is consolidated in a cube mould with a mechanically-operated hammer. The mortar has normal consistency when water just appears after 1 kg.m. of work has been expended per 10 g. of material  $\pm 5$  blows. For 800 g. dry mixture, weight of hammer 3 kg., and height of fall 0.5 m., the water should not appear before 48 blows or after 58.

*Tensile Strength Tests.*—The specimen is to have the standard 8-shape with a minimum cross section of 5 sq. cm.

For cement paste the mixing is to be done for five minutes, and six specimens are to be made together. If a Werner and Pfleiderer mixer of 5-litre capacity is used, twelve specimens may be prepared at a time. The paste is to be divided into equal parts, placed in six or twelve moulds, and smoothed with an oval spoon or a knife. In order to expel the air the mould may be rapped on the edge of the table for two minutes at 100 to 120 blows to the minute, the mould being rotated 90 deg. every half a minute. Five minutes after this the excess paste is to be removed with a wet knife. The day after gauging the specimens must be placed in water; in no case may they be kept in an unsaturated atmosphere. After 24 ( $\pm 2$ ) hours the specimens must be removed from the moulds without rapping them on a hard surface, immediately put into water, and left there for 3, 6, and 27 days. The water must be changed weekly and the temperature kept at 15 to 16 deg. C. The specimens are to be stored on edge, and the level of the water should be about 2 cm. above their upper surface.

The mortar specimens are to be made of mortar of normal consistency (1 cement to 3 sand) and should be 6 (or 12) in number, 300 (or 600) g. cement and 900 (or 1800) g. standard sand being used. The preparation is to follow that of cement

paste. The mortar is consolidated in the mould with a hammer of 2 kg. weight falling through 0.25 m. Every 10 g. of dry mixture is to have 1 kg.m. of work expended on it. After it is made, the specimen should be stood on an oiled glass plate and the free surface smoothed with a knife. It is then removed from the mould. The storing of the specimens is to be the same as for those of cement paste. The specimens may be tested in any standard testing machine. The shot must have a diameter of between 2 and 2.5 mm. and the speed of flow must be  $100 \pm 10$  g. per second. To obtain the mean breaking strength the mean of the four best out of six specimens is used. If the cement paste specimens show a shrinkage of more than  $\pm 2$  per cent. this must be taken into account in recording the breaking strength. The strengths required are as follow :

Type of Portland Cement.	Neat Cement. kg. per sq. cm.				1 : 3 Mortar. kg. per sq. cm.			
	3	4	7	28	3	4	7	28
" 000 " .. ..	30	—	40	55	18	—	23	28
" 00 " .. ..	—	25	30	45	—	12	16	22
" 0 " .. ..	—	20	25	35	—	10	12	16

**Compressive Strength.**—Compressive strength tests are to be carried out with standard 1 : 3 mortar on cubes of 7.07 cm. sides having a cross sectional area of  $50 (\pm 1)$  sq. cm. Nine cubes are to be prepared and tested, 3 after 4 (or 3) days, 3 after 7 days, and 3 after 28 days. The storage is to be the same as for tensile specimens. The strengths required are :

Type of Portland Cement.	kg. per sq. cm.			
	3 days.	4 days.	7 days.	28 days.
" 000 " .. ..	200	—	300	420
" 00 " .. ..	—	120	180	275
" 0 " .. ..	—	70	100	160

#### Pozzolana Portland Cement.

Pozzolana Portland cement is obtained by grinding Portland cement clinker with more than 10 per cent. of hydraulic materials such as pozzolana, trass, diatomaceous earth, etc. The amount of Portland cement in the product may vary between wide limits. No chemical analysis is required.

**Setting Time.**—Initial set must not be less than 20 minutes and the final set not longer than 12 hours.

**Soundness.**—The cement must be sound after hot and cold water tests.

**Fineness.**—Residue on the 900-mesh sieve must not be greater than 2 per cent. nor that on the 4900-mesh sieve greater than 20 per cent.

*Tensile Strength.*—1 : 3 mortar made with standard sand must have a strength of at least 12 kg. per sq. cm. after 7 days and 16 kg. per sq. cm. after 28 days.

*Compressive Strength.*—1 : 3 mortar made with standard sand must have a compressive strength not less than 80 kg. per sq. cm. after 7 days and 160 kg. per sq. cm. after 28 days.

*General Instructions.*—Testing must be carried out in the same way as for Portland cement.

#### Slag Portland Cement.

Slag Portland cement is obtained by grinding Portland cement clinker with granulated basic blast-furnace slag of suitable composition. The amount of slag must not exceed 85 per cent. Gypsum may be added in amounts up to 3 per cent. by weight of the mixture. Neither the  $\text{SO}_3$  nor the  $\text{MgO}$  content may be greater than 5 per cent. The  $\text{MnO}$  content in the finished product must not exceed  $x = 5 \cdot \frac{a}{100}$  where  $a$  = per cent. slag in the cement. In other respects the cement must conform to the specification for pozzolana Portland cement.

#### Roman Cement.

Roman cement is made by grinding together unsintered burnt natural or magnesia marl, artificial magnesia limestone mixtures, or dolomite with clay material. After burning this product must not fall to a powder when mixed with water. The  $\text{SO}_3$  content must not be greater than 3 per cent.

*Setting Time.*—Initial set must not be less than 15 minutes and final set not longer than 24 hours.

*Soundness.*—The cement must be sound to the cold water test after 4 days in air.

*Fineness.*—The residue on the 900-mesh sieve must not be greater than 15 per cent.

*Tensile Strength.*—1 : 5 mortar made with standard sand must have a tensile strength not less than 5 kg. per sq. cm. after 28 days in air saturated with water vapour and 3 kg. per sq. cm. after 28 days in water.

*Compressive Strength.*—1 : 5 mortar made with standard sand must have a compressive strength of not less than 15 kg. per sq. cm. after curing in moist air for 28 days and not less than 10 kg. per sq. cm. after 28 days in water.

*Sampling.*—An average sample must be taken for every 1000 barrels. In other respects the instructions for Portland cement must be followed.

*Testing.*—The methods of testing are the same as for Portland cement, except for the following alterations. 300 g. of Roman cement are to be used for the cement paste. Mortar of normal consistency is made with 1 part cement to 5 parts standard sand; the amounts used are to be 130 g. cement and 650 g. sand.

#### Standard Sand.

This specification is binding for all cement tests. The sand is to be pure quartz sand obtained from the quarry near Priwolsk on the Rjasan-Ural Railway.



It is to be washed and sieved. The  $\text{SiO}_2$  content must not be less than 97 per cent. and the amount of material which is not quartz must not exceed 5 per cent. The loss on ignition must not exceed 0.25 per cent. and the material must contain no clay or fine sand. The sand must not have a residue greater than 3 per cent. on the 64-mesh sieve and not more than 8 per cent. must go through a 144-mesh sieve. The wires from which the sieves are made must have the following dimensions—64-mesh sieve: diameter 0.4 mm., clear opening 0.85 mm.; 144-mesh sieve: diameter 0.3 mm., clear opening 0.533 mm.

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## The Composition and Properties of Portland Cement.

In the course of a paper read recently at the Society of Chemical Industry, Mr. F. M. Lea, M.Sc., A.I.C., of the Building Research Station, said the relation between the composition and properties of Portland cement had formed the subject of much discussion in recent years, and the desire to obtain cements in which some particular property had a maximum or minimum value had stimulated many investigations. The properties to which attention had been directed were those of strength, volume change (shrinkage and expansion), heat of hydration, and resistance to chemical attack.

Portland cement was produced by a clinkering process in which some 20 per cent. to 30 per cent. of the mix became liquid at the clinkering temperature. It had been shown<sup>1</sup> that if complete equilibrium was to be maintained in the cement clinker, as the Bogue calculation presupposed, some reaction between this liquid and the existing solid must in many cases occur during cooling of the clinker. It seemed that under the conditions of cement production no such reaction occurred during cooling owing to the short time available over the temperature range involved. The conception that Portland cement clinker was to be regarded as a material which closely approached equilibrium at the clinkering temperature, but in which the equilibrium was "frozen" on cooling, had therefore gained much support. On this conception, which had been discussed by the writer elsewhere,<sup>1</sup> the compound content of cements might differ somewhat from the values given by the Bogue calculation. This difference arose in the appearance of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  as one of the products of crystallisation and a resultant change in the proportions of  $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ , and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . Formulae by which the compound content of cements could be calculated on this five-compound basis ( $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$ ,  $\text{C}_5\text{A}_3$ , and  $\text{C}_4\text{AF}$ ) were now in course of publication, and might be used to replace the Bogue four-

<sup>1</sup> F. M. Lea, *Cement*, 1935, 8, 29; F. M. Lea and T. W. Parker, Building Research Tech. Paper No. 16, 1935.



compound calculation ( $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_4AF$ ). There was, however, an additional difficulty. In the calculation of compound content it was assumed that all the liquid formed in the cement clinker at the clinkering temperature crystallised on cooling. Microscopic examination of cements suggested, however, that part of this liquid might sometimes fail to crystallise and form a glass. There was at present no means by which the extent of glass formation might be estimated quantitatively, and there was little knowledge of the relative properties of glass and crystal phases of the same mean composition. Unless their properties were the same, and such evidence as was available suggested the contrary, the use of the compound contents, calculated by either the four- or five-compound method, for the analysis of data on cement properties must involve errors of uncertain magnitude.

It was well known that in general, and within certain limits, the rate of strength development of a cement tended to increase as the lime content was raised. The view had also been expressed that a high content of alumina and ferric oxide favoured the production of cements which showed a rapid development of strength. This effect of the sesquioxides was probably to be attributed primarily to their influence in cement burning rather than to the cementing qualities of the compounds they formed. It seemed that a high content of sesquioxides might facilitate commercially the production of a cement with a lime content sufficiently high to convert almost all the silica to tricalcium silicate without undue amounts of free lime remaining in the clinker. Examination of the analyses of a large number of rapid-hardening Portland cements seemed to afford little support for the view propounded by Kühl<sup>2</sup> that a high or low, but not an intermediate, value of the silica modulus (ratio  $SiO_2 : R_2O_3$ ) was most favourable to the development of high early strengths.

The results of the studies made in recent years on the relation between chemical composition and properties of Portland cement had established perhaps with the greatest success the variation of heat of hydration with the content of the various compounds. With strength the relation to the content of tricalcium and dicalcium silicate was clear in general outline, but the effect of the aluminate compounds was still uncertain. With chemical resistance a certain general relation with the content of tricalcium aluminate appeared, but with shrinkage no consistent data had been obtained.

An improved method for the calculation of the compound content of cements such as was afforded by the five-compound method should assist in clarifying certain of these relationships, but some knowledge of the amount of glass existing in cement clinker and of the relative properties of glass and crystal phases of the same mean composition seemed essential to further progress. It seemed also that, in the case of shrinkage at least, complex problems of the structure of set cements might be involved and that the assumption that the shrinkage of a cement could be regarded as the sum of the shrinkage of the individual cement compounds was of doubtful validity.

<sup>2</sup> H. Kühl, *Cement Chemistry in Theory and Practice*, Trans. by J. W. Christelow, p. 45.

## Low-heat Cement.

Some preliminary conclusions regarding the use of low-heat cement in the construction of the Boulder Dam have been published by Mr. R. F. Blanks, Engineer of the Bureau of Reclamation, Colorado. It is pointed out that these conclusions are only applicable to the conditions on this particular work and to the aggregate used.

The physical properties of the low-heat cement used for Boulder Dam are practically identical to the corresponding properties of standard Portland cement, as shown in Table I. The only difference of importance is that the low-heat

PHYSICAL PROPERTIES.

Type of cement.	Per cent. passing 200 mesh.	Specific surface sq. cm. per gr.	Spec. gravity.	Initial set.	Final set.	Normal consistency.	Water content by weight.	Slump, In.			
								1:2.9 plastic mortar.	1:5.2 $\frac{3}{4}$ in. max. agg.	1:5.75 $1\frac{1}{4}$ in. max. agg.	1:9.5 6 in. max. agg.
Standard	93.9	1795	3.16	h. m. 3-15	h. m. 5-40	23.3	.54	1 $\frac{1}{2}$	3	4 $\frac{1}{2}$	2 $\frac{1}{2}$
Low-heat	94.6	1950	3.16	2-35	5-05	22.6	.54	2	3	4 $\frac{1}{2}$	2 $\frac{1}{2}$

CHEMICAL COMPOSITION.

Type of Cement	Chemical analysis						Ignition loss	Compounds			
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>		C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF
Standard	21.8	6.2	2.9	63.8	2.6	1.7	1.1	40	32	12	8
Low-heat	23.8	5.2	4.6	60.5	2.8	1.9	1.2	18	54	6	14

cements are somewhat finer and therefore result in concrete of improved workability. The low-heat cements are characterized by high percentages of di-calcium silicate (C<sub>2</sub>S) and tetra-calcium aluminoferrite (C<sub>4</sub>AF), with relatively low percentages of tri-calcium silicate (C<sub>3</sub>S) and tri-calcium aluminate (C<sub>3</sub>A) as compared with relatively high C<sub>3</sub>S and C<sub>3</sub>A contents of standard cements.

Low-heat cements result in considerably lower temperature rise and less heat of hydration than normal cements (Fig. 1), yet the compressive strengths at 90 days are very nearly equal for both standard and mass curing (Fig. 2). Standard curing refers to continuous storage of unsealed specimens in moist rooms maintained at about 70 deg. F., and mass curing applies to specimens sealed in thin metal containers and stored in adiabatic calorimeter rooms on a

rising temperature cycle for 28 days and at 70 deg. F. thereafter. It is interesting to compare the gradual but continuous strength development of the low-heat cements with the high early strength attained by the standard cements.

The thermal properties vary between rather wide limits for the different conditions represented. The major factors accounting for the variations, in the order of their importance, are (1) rock type of aggregates with respect to mineral composition; (2) water content of the concrete mix; and (3) temperature of the concrete. The variation in specific heat for different concretes might account for 10 per cent. or more difference in the temperature rise resulting from heat of hydration of the cement in a given structure and correspondingly greater or less volume change tending toward the formation of shrinkage cracks. Similarly,

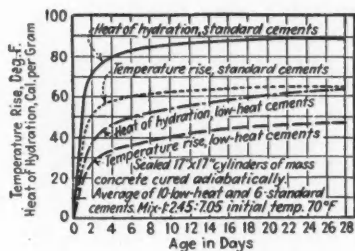


Fig. 1.

Temperature rise and heat of hydration of Low-heat and Standard Cements in mass concrete.

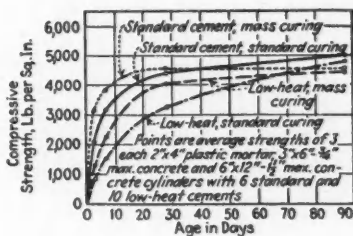


Fig. 2.

Compressive strengths (mortar and concrete) of Low-heat and Standard Cements.

concrete having high values for thermal diffusivity would be cooled through a given temperature drop in one-half the time required for concrete having a low diffusivity value represented.

The cement efficiency (unit strength per unit of cement content) is substantially the same for any given size and grading of aggregate regardless of the richness of the mix, and decreases as the maximum size of aggregates is decreased. This indicates the desirability of using 9-in. or larger stones in mass concrete. However, experience has shown that 9 in. is the largest size that can be economically and efficiently mixed and placed, and that even this limit may cause some trouble. Furthermore, there are indications that the larger the particle of aggregate the more detrimental may be the weak laitance film formed on the underside of the particles. The Bureau of Reclamation has adopted 6 in. as the maximum allowable size of aggregate for more recent work. The 5 per cent. difference in cement efficiency between 6-in and 9-in. maximum aggregate is more than compensated for in greater ease of control of mixing and placing and in improved uniformity of the finished concrete.

## Deterioration of Concrete Structures in Alkaline and Sea-water.

By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

THE deterioration of poor quality concrete or reinforced concrete with insufficient cover to the steel by exposure to sea-water is due to (a) corrosion of the reinforcement, or (b) deterioration, under certain conditions, of the concrete. Both types of deterioration usually occur above the level of complete immersion. The attack on reinforced concrete begins with the corrosion of the reinforcement just above the mean water level. Owing to the expansion accompanying corrosion the concrete covering becomes cracked, sea-water penetrates, and the attack on the metal proceeds with increasing rapidity. Splitting and peeling continue upwards from low-water level as far as the salt-laden air is found. The attack on plain concrete shows similar features and appears to originate wherever sea-water gains access below the surface skin of concrete. Cases of deterioration are quoted by Squire<sup>1</sup> in which it is confined to portions of the structure below the tide-line, although in general deterioration proceeds above and below mean water level.

Le Chatelier<sup>2</sup> stated that this deterioration was caused by the formation of calcium sulphoaluminate, and he argued that the active ingredients in the concrete can react with the magnesium salts of the sea-water by double decomposition producing calcium chloride and sulphate. The sulphate formed reacts with the hydrated calcium aluminate to form calcium sulphoaluminate. The destructive qualities of this compound are alleged to be due to its crystallization with such a large amount of water that it occupies a very much larger volume than the hydrated aluminate from which it is formed, thereby producing a strain within the structure which eventually cracks. Moreover, by extracting the alumina and lime the normal hardening process is interfered with and the result is a soft, crystalline, non-hardening mass.

The existence of calcium sulphoaluminate has been fully substantiated, but there is some question as to its exact formula and the part it plays in the deterioration of concrete structures. It may be formed (1) during the gauging of Portland cement ground with gypsum addition, (2) by gauging any calcium aluminate-gypsum mixture or by the action of some sulphate solutions on calcium aluminates, (3) by adding aluminium sulphate solution to lime-water, (4) by mixing lime-water and aluminium hydroxide with a solution of certain sulphates. A summary of the literature on the isolation and suggested composition of calcium sulphoaluminate follows.

Candlot<sup>3</sup> made this compound by the reaction between calcium sulphate and calcium aluminate (which aluminate he does not state). He found that the compound had a composition corresponding to the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4$ . It crystallized with a large number of molecules of water, and Candlot has given this number as 59.

Michaelis<sup>4</sup> considered the compound to have the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$ .

Deval<sup>5</sup> prepared the substance by (1) reaction between aluminium sulphate, calcium sulphate and lime-water, and (2) reaction between calcium sulphate and tricalcium aluminate. He arrived at the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 28.5\text{H}_2\text{O}$ . Later<sup>6</sup>, using sodium sulphate, he found that some of his calcium sulphoaluminate preparations contained more and others less calcium sulphate than the amount necessary to correspond with this formula. He concluded that the material is of indefinite composition, depending on various factors such as the  $\text{SO}_3$  concentration, per cent.  $\text{Al}_2\text{O}_3$  present, and the activity of the reacting lime.

Klinkenberg<sup>7</sup> prepared sulphoaluminates from "dicalcium aluminate" and calcium sulphate and gave their composition as  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12.5\text{H}_2\text{O}$ ,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot 18.3\text{H}_2\text{O}$ , and  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 19.5\text{H}_2\text{O}$ .

Bates, Phillips and Wig<sup>8</sup> failed to obtain a body of the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$ . By treatment of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  with a solution of plaster of Paris they obtained a body of the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4$ , but failed to obtain anything approaching this formula when using mono- or "di-" calcium aluminate. They found that sodium-calcium-sulphoaluminate did not exist, nor did sulpho-silicates.

Nitzsche<sup>9</sup> found a double sulphate of lime and alumina is always formed when a solution of a sulphate is brought into contact with lime-water, but that it is only stable in the presence of lime-water. Klein and Phillips<sup>10</sup> prepared a body of the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ , where  $x$  varies with the drying conditions.  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  is shaken with water and the suspension rapidly filtered, the filtrate running into a clear saturated calcium sulphate solution. A solution of calcium hydroxide is added and a white, apparently gelatinous, precipitate forms which on microscopic examination is seen to be a homogeneous mass of minute prismatic crystals. In order to increase their size the solution was allowed to evaporate spontaneously in a vacuum desiccator over sulphuric acid until it was reduced to one-third its original volume. It was then rapidly filtered, washed with calcium hydroxide solution and ethyl alcohol, and air-dried for two hours. Analysis showed the crystals corresponded with the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 36.5\text{H}_2\text{O}$ . Another sample was dried on the filter-pump, and gave an analysis corresponding with the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 42\text{H}_2\text{O}$ . These crystals are optically identical with those obtained by gauging calcium aluminate-gypsum mixtures with water. They are long prisms with no twinning. Optically their characteristics are bi-axial and positive, parallel extinction, refractive index less than 1.48, and a large optic axial angle. The crystals are very easily distinguished from  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  by (1) lower double refraction, (2) different optical character of principal zone, and (3) different prismatic development.

The variation in water content as found by different workers indicates the great ease with which water is lost. The crystals cannot be dried at 100 deg. C., for they then decompose with the formation of hydrated calcium aluminate and

peculiar club-shaped crystals of calcium sulphate<sup>10</sup>. The optical properties of these crystals suggest a composition somewhere between that of anhydrite and gypsum, since the refractive index and double refraction of the crystals are both greater than those of gypsum but less than those of anhydrite.

According to Mecke<sup>11</sup> there are two different calcium sulphoaluminates, viz.,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4$ . The latter is stated to be formed by the action of lime water and "dicalcium aluminate" on the former. In addition to differing in molecular composition, the two sulphoaluminates differ in optical properties, crystal form, resistance to lime and soda, and solubility.

Lerch, Ashton and Bogue<sup>12</sup> have also prepared two different sulphoaluminates, viz.,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ . The former was prepared in a similar manner to that used by Klein and Phillips<sup>10</sup>, but  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  was used instead of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The optical properties of the product were very different, however, the crystals being needle-shape but uniaxial with negative interference figure. Refractive index by the immersion method was  $w_D \dots 1.464$  and  $e_D \dots 1.458$ . Its density at 20 deg. C. is given as 1.48. On heating to 110 deg. C. the water content is reduced to  $7\text{H}_2\text{O}$  and then remains constant. Judging by the similarity between the optical and other properties of this substance and those of the natural calcium sulphoaluminate "ettringite"<sup>40</sup>, the two are apparently identical.

The other sulphoaluminate is prepared by adding 200 c.c. of saturated lime water to 500 c.c. of a 2 per cent. solution of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and filtering. On the addition of 200 c.c. of saturated calcium sulphate solution to the filtrate, hexagonal crystals corresponding to the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$  separate out. These show negative uniaxial interference figures, with refractive index  $w_D \dots 1.504$  and  $e_D \dots 1.488$ . Its density at 20 deg. C. is given as 1.95. On heating to 110 deg. C., the water content is reduced to  $6\text{H}_2\text{O}$ . It is unstable in water and tends to pass into the stable form  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ , but the transformation is slower in lime water than in plain water. The more stable form is, however, somewhat hydrolysed in water and is only really stable in gypsum and lime solutions. Appreciable hydrolysis occurs in  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  solutions, while solutions of  $\text{Na}_2\text{CO}_3$  and  $\text{MgSO}_4$  completely destroy it, forming  $\text{CaCO}_3$  and  $\text{CaSO}_4$ . The authors state that  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 21\text{H}_2\text{O}$  is the compound formed on gauging cement-gypsum mixture with water.

Shelton<sup>13</sup> found that calcium sulphoaluminate crystals are abundantly formed by the action of dilute sodium sulphate and dilute magnesium sulphate solutions (below 0.1 mol. per litre) on calcium aluminates. These reactions occur when the aluminates are suspended in the sulphate solutions. Strong solutions of  $\text{MgSO}_4$  do not result in the formation of sulphoaluminate, but of gypsum crystals.

Koyanagi<sup>14</sup> says that calcium sulphoaluminate has the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$  and is formed by either gauging a cement containing gypsum or by treating a sound cement for 8 to 14 hours with 30 times its weight of water. After filtering and adding a saturated solution of calcium sulphate to the filtrate, the mixture is allowed to crystallize. Later<sup>15</sup> he modified his view and claims to



have experimentally demonstrated that calcium sulphoaluminate has the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{CaSO}_4 \cdot y\text{H}_2\text{O}$  where  $x$  and  $y$  vary according to the concentration of gypsum used in the preparation of the substance,  $x$  varying from 0 to 3 and  $y$  from 10.62 to 32.61. Koyanagi has observed all the following sulphoaluminates by varying the  $\text{SO}_3/\text{Al}_2\text{O}_3$  ratio in his experimental preparations:  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  (Michaelis),  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  (Candlot),  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot n\text{H}_2\text{O}$  (Mecke), and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$  (Lerch, Ashton and Bogue). He also states that only the form with the composition  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32.6\text{H}_2\text{O}$  develops in the hydration of Portland cement containing gypsum.

Table I below shows the optical properties of sulphoaluminates as found by various workers mentioned in this article and Table II gives the formula for calcium sulphoaluminate believed by various investigators to be present in hydrated Portland cement.

TABLE I

	Klein and Phillips <sup>10</sup> .	Shelton <sup>13</sup> .	Lerch, Ashton and Bogue <sup>12</sup> .		Koyanagi <sup>14</sup> .
			High sulphate shape	Low sulphate shape	
Formula	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$	Not given	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32.6\text{H}_2\text{O}$
Crystal shape	Long fine needles, often in spheruliths.	Long needles and prisms.	Long fine needles often in spheruliths.	Hexagonal plates.	Prisms. With low gypsum concentration, long fine needles also in spheruliths
Optical properties.	Bi-axial. Positive.	Bi-axial. Positive.	Uniaxial. Negative.	Uniaxial. Negative.	Uniaxial. Negative.
Extinction	Parallel	Parallel	Parallel	Parallel	Parallel
Coefficient of refraction	Less than 1.48	w 1.461 ± .003 e 1.463 ± .003	w 1.464 ± .002 e 1.458 ± .002	w 1.504 ± .002 e 1.488 ± .002	w 1.465 ± .002 e 1.461 ± .002
Double refraction	Weak	0.002	0.006	0.016	0.004

O'Hara<sup>16</sup> expressed the same opinion as Le Chatelier as to the cause of deterioration in sea-water, but also stated that the magnesium hydrate liberated during the process has a tendency to fill the voids and produce a denser concrete which would exclude the sea-water. Thus disintegration would eventually be retarded if the concrete were not too porous originally. He states that concrete which has failed in sea-water is usually found to contain a high percentage of magnesia. Candlot<sup>17</sup> put forward the theory that a calcium chloroaluminate is formed as an intermediate product in the formation of calcium sulphoaluminate. Poirson<sup>18</sup> prepared a calcium chloroaluminate in a number of ways and gave as its formula  $2(3\text{CaO} \cdot \text{Al}_2\text{O}_3) \cdot \text{CaCl}_2$ . It is unstable in pure water and decomposes

TABLE II

Author.	Date.	Formula.
Candlot .. .. .	1890	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 59\text{H}_2\text{O}$
Michaelis .. .. .	1892	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{H}_2\text{O}$
Schott .. .. .	1894	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot 18\text{H}_2\text{O}$
Klinkenberg .. .. .	1895	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12.49\text{H}_2\text{O}$
Klinkenberg .. .. .	1895	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot 18.25\text{H}_2\text{O}$
Klinkenberg .. .. .	1895	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 19.55\text{H}_2\text{O}$
Rebuffat .. .. .	1896	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 10\text{H}_2\text{O}$
Rebuffat .. .. .	1896	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 10\text{H}_2\text{O}$
Deval .. .. .	1900	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
Rebuffat .. .. .	1902	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$
Poirson .. .. .	1910	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
Klein and Phillips .. .. .	1914	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
Kühl and Albert .. .. .	1923	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
McIntire and Shaw .. .. .	1925	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
Lerch, Ashton and Bogue .. .. .	1929	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$
Lerch, Ashton and Bogue .. .. .	1929	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$
Mecke .. .. .	1929	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{CaSO}_4 \cdot n\text{H}_2\text{O}$
Koyanagi .. .. .	1931	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32.6\text{H}_2\text{O}$

in solutions of sulphates with the formation of calcium sulphoaluminate. Potter<sup>19</sup> found that magnesium salts are the cause of the disintegration of concrete in sea-water, but he also agrees with Le Chatelier that calcium sulphoaluminate is formed and crystallizes with expansive force. Meyer<sup>20</sup> reports that the calcium sulphate, formed by double decomposition between the magnesium sulphate of the sea-water and the hydrated lime set free in the concrete, reacts with the hydrated tricalcium aluminate to give the sulphoaluminate of the formula  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 26.5\text{H}_2\text{O}$ . The formation of this compound is accompanied by a considerable increase in volume, thereby causing cracks in the concrete. When free hydrated lime is no longer present the sulphoaluminate reacts with magnesium sulphate and chloride with the formation of aluminium hydroxide, magnesium hydroxide, calcium sulphate, and calcium chloride.

Le Chatelier<sup>2</sup> suggested that, in order to avoid the formation of excessive quantities of sulphoaluminate, cements for sea-water work should have the alumina replaced in part by iron oxide. These "iron" cements proved satisfactory, yet it was felt that Le Chatelier's explanation could not be altogether correct in view of the high resistance to sea-water of aluminous cements. The following arguments were therefore put forward in opposition to the sulphoaluminate theory.

(a) Klein and Phillips<sup>21</sup> stated that disintegration is due to the crystallization of calcium sulphoaluminate but has been greatly exaggerated, for although it crystallizes with large quantities of water the crystals produced in a hydrated cement are extremely small. Microscopic examination of hydrated cements shows that the maximum length of the crystals of sulphoaluminate never exceeds 0.04 mm., and their width never exceeds 0.0025 mm., so that a suspension of the crystals has the appearance of a gelatinous precipitate. The crystals are small owing to their immediate precipitation from solution on coming in contact with lime water, and only increase in size to a small extent.

Jewett<sup>22</sup> noted that failure of concrete work in alkali water was caused by the formation of crystals with enormous expansive force, so that Klein and Phillips maintain that they could not be sulphoaluminate crystals.

(b) Endell<sup>23</sup> points out that synthetic calcium sulphoaluminate is decomposed by sodium chloride, magnesium chloride solutions, and sea-water, and its formation in the presence of sea-water is therefore improbable. Lerch, Ashton and Bogue<sup>12</sup> also found that appreciable hydrolysis of sulphoaluminate occurs in sodium chloride and magnesium chloride solutions, while solutions of sodium carbonate and magnesium sulphate completely destroy it.

(c) Shelton<sup>24</sup> points out that when crystalline hydrated tricalcium aluminate is acted upon by magnesium sulphate solutions the grains become protected by a coating of magnesium hydroxide, which stops further action. Later<sup>25</sup> he examined the action of solutions of sodium sulphate and magnesium sulphate on suspensions of hydrated Portland cement. The crystals of calcium hydroxide and hydrated tricalcium aluminate rapidly disappear with the formation of amorphous masses of gel which subsequently become granular. No sulphoaluminate crystals were produced by the action, those already present being formed from the gypsum present in the cement.

(d) By studying the variation of  $\text{CaO}$  and  $\text{SO}_3$  contents of the liquid and solid phases of a suspension of cement in solutions of the chlorides and sulphates of sodium and magnesium, Bates, Phillips and Wig<sup>26</sup> concluded that calcium sulphoaluminate was not responsible for the deterioration of concrete in these solutions.

(e) Rebuffat<sup>27</sup> concluded that for concrete in sea-water the formation of calcium sulphoaluminate is at most transient and can take place only to a small extent, and therefore it has only a very slight action on the stability of the cement.

(f) Nitzsche<sup>28</sup> showed that calcium sulphoaluminate is not produced by immersing test concrete mortars in artificial sea-water. Neither did he find it when test-blocks were immersed in sea-water, but it was found when they were placed in dilute sulphate solutions. He thus concluded that deterioration of concrete by surface waters and by peaty and alkaline waters is due to the formation of sulphoaluminate, but not in the case of sea-water. Passow<sup>29</sup>, on the other hand, did not observe the formation of calcium sulphoaluminate in cement tests destroyed by sulphate solutions. He agrees that it might have been formed during the early stages and disappeared later, but considers the cause of disintegration to be the formation of needle crystals of gypsum.

Apart from these arguments put forward in opposition to the sulphoaluminate theory, there appears to be a general agreement that in the presence of sea-water and similar sulphate-chloride solutions, the most soluble element in cement is lime. According to Bates, Phillips and Wig<sup>26</sup> the quantity of silica, alumina, and iron present in cement does not affect the solubility of the lime and the magnesia in the sea-water is precipitated in direct proportion to the solubility of the lime. In their investigations on the effect of various solutions on cement they found that, judging by the amount of lime abstracted from the cement,

cements are more readily attacked by chloride solutions of sodium and magnesium than by the corresponding sulphate solutions. The amount of  $\text{Mg}(\text{OH})_2$  precipitated by cements from solutions of the chlorides and sulphates of magnesium is large at first, but the rate of precipitation decreases rapidly with time. Unless sodium carbonate is present the silica and iron oxide content of the cement are unaffected by the process, but there appears to be a slight loss of alumina and a slight gain of chloride by the cement. These conclusions were also confirmed when sea-water was used. The quantity of chlorine and sodium taken up by the cement is so small that no statement can be made as to the existence of any definite chloride or sodium compound formed with the cement. They found, however, that the action upon cement structures of the sulphates present in sea-water is much accelerated by the presence of chlorides. Steck<sup>30</sup> also observed this effect, and in addition found that sodium carbonate decreases the harmful effect of sulphate. He regards magnesium chloride in the sea-water as having a greater disintegrating effect than sulphates since it gives rise to calcium chloride which is leached out, forming pores, thus weakening the structure and leading to further attack. He concluded that the formation of compounds having molecular volumes larger than that of  $\text{Ca}(\text{OH})_2$  is not the cause of disintegration of the concrete, but that disintegration is due to the formation of compounds which are subsequently removed from the structure by solution. Bates, Phillips, and Wig also found that air curing cement before placing it in contact with the sea-water, thereby carbonating the lime at or near the outer surface of the structure, did not prevent disintegration. While this carbonated coat may be immune or very slowly affected, it is permeable, and the uncarbonated portion within may be attacked and result in the peeling off of the carbonated surface. The  $\text{Mg}(\text{OH})_2$  replaces the lime but has no cementitious value, with the result that the cement will lose its strength and the structure will crumble.

O'Hara<sup>16</sup> found large quantities of  $\text{MgO}$  occurred in concrete structures which had been destroyed by the action of sea-water. Other authors maintain that calcium sulphate in considerable quantities is found when concrete is placed in sea water. As this compound has no setting properties under the conditions, the mass may be washed away by stream or wave action. Attwood and Johnson<sup>31</sup> are of opinion that this calcium sulphate is formed by the action of the sulphates present in sea water upon the free hydrated lime of the set cement and not by double decomposition between the sulphate solutions and the silicates and aluminates present in the cement.

Thorvaldson, Harris, and Wolochow<sup>32</sup> have investigated this theory and their experiments show that solutions of sodium sulphate extract  $\text{Ca}(\text{OH})_2$  from concrete, but the amounts of silica and alumina removed are very small; 84 per cent. of the  $\text{Ca}(\text{OH})_2$  present can be extracted with successive quantities of a 1.64 per cent. solution of sodium sulphate. Solutions of calcium chloride slightly inhibit this extraction, while sodium chloride solutions have an accelerating effect. Thorvaldson came to the conclusion that there are three stages in the attack on

cement by sulphate solutions, namely, (1) direct reaction between the free hydrated lime and the sulphate, e.g.,  $\text{Ca}(\text{OH})_2 + \text{Na}_2\text{SO}_4 = 2\text{NaOH} + \text{CaSO}_4$ ; (2) this removal of hydrated lime speeds up the liberation of more lime from the cement, which in turn reacts with the sulphate so that eventually there is development of abnormally high alkalinity due to NaOH; (3), a second reaction then sets in involving  $\text{CaSO}_4$  formation, without increasing the alkalinity owing to the direct displacement of the lime in the aluminates and silicates by sodium. It is this reaction which Thorvaldson considers produces the disintegration of the cement.

In connection with this formation of  $\text{CaSO}_4$ , tests have been made on the resistance to sea water of cements with increased  $\text{SO}_3$  content. Goslich and Dyckerhoff<sup>33</sup> showed that the addition of  $\text{CaSO}_4$  to cements, if not excessive, increases the strength of the concrete whether it is placed in fresh or sea water. Tests tabulated on high and low  $\text{SO}_3$ -content cements show that the presence of 2.5 per cent.  $\text{SO}_3$  is harmless during hardening in sea water. Two cements were used for further tests, one with an  $\text{SO}_3$  content of 1.19 per cent. and another with  $\text{SO}_3$  content of 0.5 per cent. A sample of each was enriched to an  $\text{SO}_3$ -content of 2.5 per cent. The examination of blocks made from each of these cements after being subjected to tidal action on an island in the North Sea showed that the high  $\text{SO}_3$  sample behaved well before and after enrichment to 2.5 per cent.  $\text{SO}_3$  content, while the low  $\text{SO}_3$  sample behaved poorly and was improved by the addition of gypsum to bring the  $\text{SO}_3$  content up to 2.5 per cent. Chemical examination showed very slight alteration in sea water in the high  $\text{SO}_3$  samples, but there were extensive changes in the low ones. These experiments appear to indicate that the presence of  $\text{SO}_3$  up to the amounts usually present in commercial cements is not detrimental, but is rather an advantage where the cement is to be used for marine work.

As most cases of deterioration occur where the concrete is exposed to strong tidal or other intermittent action of the salt water, another theory has been advanced. Fisk<sup>34</sup> believes that physical as well as chemical causes can bring about deterioration. The mechanical action of the crystallization of the salts from the water absorbed by the outer layer of the concrete produces expansion and deterioration begins. If the salts take up water of crystallization there is greater expansion. With each repeated wetting and drying more and more crystallization occurs, and eventually particles on the surface are detached and the disintegration becomes apparent. Another fact which has a bearing on this subject is the tendency of crystals to grow in certain directions, and this tends to increase the penetration as well as to accentuate the destructive effect.

Before concluding the chemical aspect of the deterioration of concrete in sea water, mention should be made of the studies by Thorvaldson and co-workers<sup>32, 35, 36</sup> of the action of sulphate solutions on the aluminates and silicates of calcium present in Portland cement. The effect of sulphate solutions was observed by following the expansion of a bar, and by the decrease in tensile strength with time, when the bars were immersed in sulphate solutions. Thor-

valdson<sup>35</sup> found that mortars made from pure  $3\text{CaO} \cdot \text{SiO}_2$  and pure  $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$  are not disintegrated in solutions of  $\text{Na}_2\text{SO}_4$ , but expand and are disintegrated in solutions of  $\text{MgSO}_4$ . If  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  is added to either, the resulting mortar disintegrates rapidly in solutions of both magnesium and sodium sulphates. Steam treatment was found to increase greatly the resistance of cement mortars to the disintegrating action of sulphate solutions. Thorvaldson stated that this was due to the formation of a stable hydrated calcium aluminate. He stated also that this hydrated aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , is obtained by steam curing of the set aluminate under pressure at 125 to 175 deg. C. for four hours. The hexahydrate was isolated in isotropic crystals of  $n_D = 1.604 \pm 0.0002$  and is undoubtedly different from that obtained by Klein and Phillips<sup>10</sup>. Thorvaldson contends that this hexahydrate is more stable than the normal hydrated calcium aluminate, and its formation accelerates a reaction of the free hydrated lime and the other compounds of the set concrete so that direct reaction between the free hydrated lime and the sulphates in the solution is rendered impossible.

Concrete structures prepared from cements of widely differing chemical composition (e.g., Portland, aluminous, and iron cements) have been found to withstand the action of sea water for many years, so it would appear that at any rate some factor other than a chemical one must also be considered.

Bates, Phillips, and Wig<sup>26</sup> showed that a pervious mortar or concrete can be destroyed by almost any salt if a sufficient amount of it is allowed to accumulate in the pores in crystal form. The drying out or seepage is a necessary part of the process since no internal stresses are set up until crystallization has occurred. This indicates why so many of the cases of disintegration reported occur at the mean water level, and is a definite indication that porous concrete is one of the causes of disintegration. Specimens of poor concrete show signs of disintegration at the mean water level but have proved durable in their lower portions which are permanently immersed. Creighton<sup>36</sup> has investigated several failures of this nature and has found them to originate in the majority of cases above the mean water level, but gradually the disintegration increases both above and below this line. In the case of porous concrete used in reinforced concrete work, the salts in sea water are able to penetrate to the reinforcement and exert a disintegrating action which, owing to the attendant expansion, gradually weakens the concrete and causes it to crack and split and in some cases to fall away from the reinforcing rods.

Thorvaldson, Wolochow and Vigfusson<sup>37</sup>, as a result of experiments on rich and lean mixtures of different brands of cement and standard sand, showed that (1) the resistance to sulphate solutions increases rapidly with the richness of mix, (2) the superiority of good quality cement is more evident with richer mixes, and (3) the increase in resistance with richness of mortar is more evident when graded sand is used.

These conclusions are also born out by Bates, Phillips, and Wig<sup>26</sup> who state that properly-made Portland cement concrete, having a dense and homogeneous surface, when totally immersed is not subject to decomposition by the chemical



action of sea water or alkali salts. The same conclusions are true with respect to partially immersed concrete exposed to tidal influence. They finally arrived at the conclusion that the physical qualities of the cement and concrete rather than their exact chemical composition determine the resistance to disintegration. The use of rich mixtures not only produces a denser concrete throughout, but also forms an impervious skin or protective coating. This may subsequently be assisted by the deposition of shells on the surface.

Poulson<sup>38</sup> made extensive experiments with mortar cubes and concrete blocks partly or wholly immersed in the Atlantic and Baltic Sea. By this means he was able to examine the effects of various climatic conditions upon concrete structures. His final conclusions were (1) the chemical action of salt water is not alone able to deteriorate Portland cement mortars, and (2) the deterioration is due almost entirely to mechanical action resulting from (a) abrasion by sand or other floating bodies in the water, (b) mechanical action of the waves, (c) frost action. Deterioration by frost only occurs in the part of the concrete which lies between the tidal ranges. Fear of deterioration by mechanical action is considerably reduced when the concrete is dense.

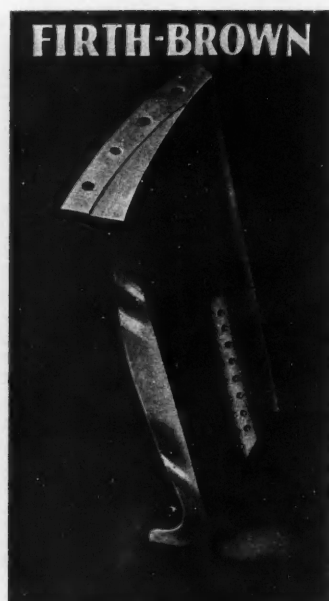
From this survey it appears that care must be exercised both in the choice of materials and in mixing when structures are to be placed in sea water or other alkali salt bearing waters. Choice of a resistant cement combined with a rich mix and carefully graded aggregate will, with good mixing, in the majority of cases, give a dense concrete resistant to action by these waters. Where the choice is confined to cements having a high lime ratio, those with high silica ratios are to be preferred. Alternatively siliceous material, such as pozzolana, trass, brick dust, etc., may be mixed with the aggregate. Such materials reduce the porosity of the concrete, but Atwood and Johnson<sup>31</sup> state that their chief action is to convert the lime set free by the action of water on the cement into a compound which is not attacked by the salts present in the sea water.

Graf<sup>39</sup> states that the addition of trass to cement mortars may have one of two effects according to the fineness of the cement used. If the cement is coarse trass addition causes an increase in strength, but if good quality fine cement is used, the addition of trass causes a fall in strength of the mortar. Many patents have been granted for claims stated to render concrete impermeable to sea and alkaline waters. These fall under two headings, namely, fillers and surface coatings. The fillers consist mainly of pozzolana, trass, brick dust, burnt clay, and granulated slag, and the quantities to be added vary from 5 to 50 per cent. of the cement. With the object of rendering the concrete waterproof, coatings of bitumen, asphalt, or tar have been applied, but such treatment, though in some measure effective, is usually costly. Facing with granite has also been recommended. Application of these materials would appear to be unnecessary if care is taken in producing dense concrete. Then, provided the concrete is not subjected to climatic extremes or mechanical stresses before it has had time to harden, it will have a high resistance to the destructive action of sea or other alkaline waters.

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**Dolomite Mortar.**—By L. Holleck. [*Tonind. Zeit.*, pp. 1093/1095 (1934)].—High strengths can be obtained with mortar made from dolomite. When burned at 850 deg. C. to a loss on ignition of 20 per cent. the dolomite gives a mortar which is several times stronger than that obtained with white lime. This type of dolomite-lime has the approximate composition  $3\text{MgO} : 2\text{CaO} : 2\text{CaCO}_3$ . If more  $\text{CO}_2$  is driven off the strength falls.

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## Note from the Foreign Press.

**The Setting and Hardening of Portland Cement.** By K. Koyanagi. *Zement*, p. 705, 1934.—The disadvantages of microscopical methods in the investigation of the setting and hardening of cement are that the material cannot be examined at early dates and that thin sections are spoilt by atmospheric carbon dioxide before they can be mounted. A method has been developed by which the fraction from a cement smaller than  $10\mu$  in diameter is separated by sedimentation in absolute alcohol and mixed with 40 per cent. water. The mixture is placed on a microscope slide and a cover glass pressed on. Sections can be obtained  $10\mu$  and less in thickness and can be protected from atmospheric action. The behaviour of various cements and the effect of various additions have been examined. The sections are examined between crossed nicols. After the specimen has been prepared the crystals of cement gradually disappear and the field becomes dark; after five to six hours a few points of light are observed which in about twelve hours may be recognised as crystals; later they grow bigger to form hexagonal plates and prisms. After about three days the whole field of view is filled with crystals. With high-early-strength cements the formation of crystals is much quicker than with ordinary cement and they are much smaller and more numerous.

A similar effect is seen on the addition of calcium chloride to ordinary cement. When a minute amount of sugar is added it stops the formation of crystals until fourteen days have passed, and even at this period they are very small and poorly developed. It was found that during the setting of cement there was practically no crystal formation. Crystal formation occurs during the hardening period, and the crystals consist of calcium hydroxide. From this it is seen that the hardening of cement is due to the crystallisation of calcium hydroxide.

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